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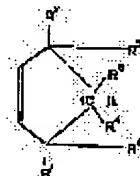
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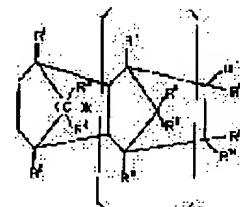
(54) MICROPOROUS POLYESTER RESIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a translucent or opaque film which is excellent in writability with a pencil and in heat resistance by stretching, at a specified temp., a film based on a compsn. contg. a thermoplastic resin and a specified amt. of a polymer obtd. by the polymn. of a specific cycloolefin and having a specified wt. average mol.wt. to thereby impart a specified void content to the film.



SOLUTION: A resin film based on a compsn. prep'd. by compounding 100 pts.wt. thermoplastic polyester resin with 5-80 pts.wt. vinylene polymer obtd. by the polymn. of a cycloolefin of formula I or II and having a wt. average mol.wt. of 800-7,000 and a glass transition temp. of 120-270°C is stretched at a temp. lower than



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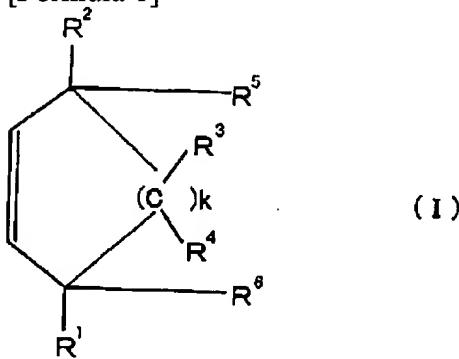
CLAIMS

[Claim(s)]

[Claim 1] As opposed to the thermoplastic-polyester system resin (A) 100 weight section The annular olefin shown by the following formula (I) or (II) a polymerization -- carrying out -- making -- obtaining -- having -- weight average molecular weight -- 800 - 7,000 -- and -- a glass transition point -- 120 - 270 -- degree C -- it is -- annular -- an olefin -- a vinylene -- a polymer -- (B) -- five - 80 -- a weight -- the section -- having blended -- a resin -- a constituent -- a base material -- ** -- carrying out -- a resin -- a film -- The following formula which is temperature lower than the melting point of a component (A), and is extended and obtained at temperature lower than the glass transition point of the vinylene of the annular olefin of (B) component [a-one number]

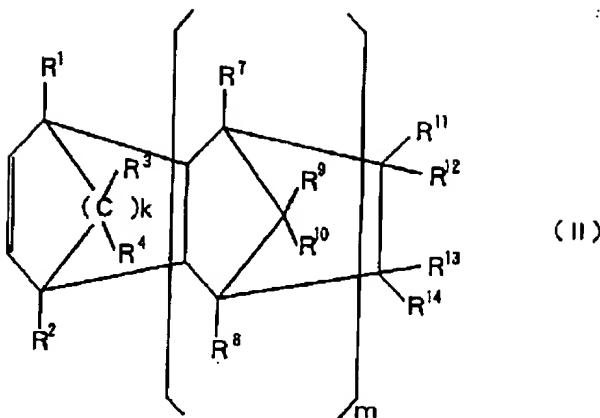
$$\text{空孔率 (\%)} = \frac{\text{(延伸前のフィルムの密度} - \text{延伸後のフィルムの密度)}}{\text{延伸前のフィルムの密度}} \times 100$$

The fine porosity polyester system resin film whose rate of a hole come out of and shown is 20 - 70%.
[Formula 1]



(R1-R4 show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) R5 and R6 are hydrogen atoms, and k is the integer of 0, or 1-4.

[Formula 2]



(R₁-R₄, and R₇-R₁₄ show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) Either [R₁₀ and] R₁₁-R₁₄ either [either / R₉ and / R₁₁-R₁₄ and] may be connected mutually, and they may form the ring. k is the integer of 0, or 1-4. m is the integer of 0, or 1-8.

[Claim 2] The fine porosity polyester system resin film according to claim 1 whose opacity (JIS P-8138) is 20% or more.

[Claim 3] As opposed to the thermoplastic-polyester system resin (A) 100 weight section being according to claim 1 -- a glass transition point -- 120 --- 270 -- degree C -- it is -- annular -- an olefin -- a vinylene -- a polymer -- (B) -- five --- 80 -- a weight -- the section -- and -- an olefin -- a system -- a resin -- (C) -- three --- 100 -- a weight -- the section -- having blended -- polyester -- a system -- a resin -- a constituent -- a base material -- ** -- carrying out -- a resin -- an And the fine porosity polyester system resin film extended and obtained at temperature lower than the glass transition point of the vinylene polymer of the annular olefin of a component (B).

[Claim 4] vinylene polymer (B)5-80 of the annular olefin the thermoplastic-polyester system resin (A) 100 weight section and whose glass transition point according to claim 1 are 120-270 degrees C -- a weight -- the section -- To the constituent which carries out olefin system resin (C) 3-100 weight section inclusion, further Molecular weight less than 10,000 or more 1,000 low-molecular-weight-polyethylene resin (D) 1 - 10 weight section, The resin film which makes a base material the polyester system resin constituent which carried out 1-10 weight section combination of the bisphenol type epoxy resin (E) The fine porosity polyester film according to claim 3 which comes in a film to form the detailed hole which is temperature lower than the melting point of a component (A), and is extended and acquired at temperature lower than the glass transition point of the vinylene polymer of the annular olefin of a component (B).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the polyester system resin film which contains a detailed cavity so much inside a film. This fine porosity polyester system resin film is translucent or opaque, and can perform clear printing and printing. Therefore, it is useful as a base material of forms, such as an outdoors poster form, a label paper, drawing paper, a sticker form, a barcode form, and printing paper, and a thermographic recording paper and hot-printing picture image acceptance paper.

[0002]

[Description of the Prior Art] Since the fine porosity resin film (JP,46-40794,B, the U.S. patent specification of No. 3,841,943) represented by the synthetic paper which makes synthetic resin a resin base material is excellent in durability, hygroscopicity-proof, dimensional stability, a surface stability, the glossiness of printed matter and clear nature, a mechanical strength, etc. compared with the paper-milling paper which uses natural pulp as the main raw material, it is used for various intended use, such as a base material of a poster form, ******, a map paper, and a thermographic recording paper, in recent years taking advantage of the characteristic feature.

[0003] Since thermal resistance is highly equipped with the demand property important as a fine porosity resin film that the waist is strong, the polyester system resin which there is polyolefine system resins, such as polyethylene and polypropylene, or a polyester system resin, and is represented by the polyethylene terephthalate especially as a base-material resin raw material of a fine porosity resin film is used for large domains, such as a thermographic recording paper and a thermal-transfer-recording picture image acceptance paper base material label.

[0004] Thermoplastic polyester resin is used as the main raw material, and the technique of split-face-izing by the technique of making a cavity detailed inside (1) film containing so much, the method of preparing the pigment coating layer which contains blast-cleaning processing, the technique of carrying out chemical etching processing and split-face-izing, (3) matte agent, and a binder for the front face of a (2) usual transparent polyester film in a film front face, etc. etc. is mentioned as technique of obtaining a film equipped with the function similar to pulp paper-milling Among these, the technique of (1) is excellent in the point that moderate flexibility can be given, compared with the technique of (2) and (3) while it is excellent in lightweight-ization of a film, and it can bring printing / imprint nature clearer than it, and promising ** is most carried out now.

[0005] As the technique of (1), gas or a vaporizable physical foaming agent is specifically added to (b) polyester system resin. the technique (for example, JP,50-38765,A and JP,57-46456,B --) of carrying out the extrusion foaming of this A chemistry foaming agent is added to JP,57-34931,A and (b) polyester system resin. How to carry out the extrusion foaming of this (for example, JP,52-43871,A, JP,58-50625,B), the technique (for example, JP,51-34963,A --) of extracting the aforementioned matter by the solvent after adding the matter ***** to a solvent to (c) polyester system resin and film-izing this to it A non-dissolving resin is mixed to JP,52-27666,B and (d) polyester system resin, melting kneading of

this is carried out with an extruder, and after forming the film which distributed this ***** resin into a polyester system resin, the technique of extending this etc. is learned.

[0006] However, no such technique is almost put in practical use. As the ground, although it is possible to make a void generate in a polyester system resin film by such technique, it is not only easy to become a big and rough void, but the control of the size is very difficult and the spatial distribution tends to become uneven. Or the fraction with an extremely low intensity occurs in a polyester film, and it is mentioned that a disconnection of a film tends to happen at the time of extension etc.

[0007] Especially in the technique of (d), when blending a resinous principle [**** / un-], since dispersibility is generally bad, if the polymer / **** / un-] of a polyester system resin and a melt viscosity which is greatly different has much amount of the polymer / **** / un-] used, it will form big and rough grain in the interior of a film, it forms a huge hole by extension, **** arises at the time of printing, or crease **** generates it. Moreover, an extension molding-temperature region becomes narrow. Conversely, if there is little amount of the non-dissolving polymer used, the light transmission of the oriented film obtained will be high, and an opaque thing will not be obtained.

[0008] As opposed to the polyester system resin which can make a film discover a cavity that the above technical problems should be solved as a non-dissolving resin (it is hereafter described as a cavernous manifestation agent) Although many polyolefine system resins (for example, JP,49-134755,A), polystyrene system resins (for example, JP,49-2016,B, JP,54-29550,B, etc.), polyarylate resins (for example, JP,58-28097,B), etc. are reported If it carries out from viewpoints, such as porosity ability, the low density nature of the synthetic paper obtained, and economical efficiency, using polypropylene resin and a polystyrene system resin will be recommended.

[0009] However, in order for the film obtained to obtain clearer printing / printing nature, it is necessary to use a cavernous manifestation agent so much, and in the case of the film using such a conventional cavernous manifestation agent, the thermal resistance of a porous film falls.

[0010] Moreover, as for the film of a publication, the size of a cavity has 50-100 micrometers and the problem of the thermal resistance of a polyester system resin porosity film falling, since it is large in JP,63-168441,A by becoming by the maximum, for example. If such a porous film is used for a thermal recording material, many the curl and wrinkleings by heat will occur.

[0011] Then, that the size and thickness of a cavity should be rationalized, in order to make the path of a cavity small, the technique of extending a polyester system resin and the film which added the surfactant, the polyalkylene glycol, etc. for the polypropylene material of a cavernous manifestation agent is indicated by JP,3-76727,A. However, since the thermal resistance of a porous film will fall if such a low molecular weight constituent is mixed, under a condition which the hot heat of a die head conducts to the base material of the recording paper like thermal ink transfer printing, a hot printing, and a sublimation imprint at the time of printing record, the problem that curl and a wrinkling occur is in the fraction.

[0012]

[Problem(s) to be Solved by the Invention] It is in offering the fine porosity polyester system resin film to which this invention is made in view of the trouble by addition of the above low-molecular-weight objects, the purpose has neither the curl by heat, nor occurrence of a wrinkling when it uses for base materials, such as a sublimating-dye-transfer-recording material, a thermal-transfer-recording material, and a thermal recording material, opacity goes up by addition of a little cavernous manifestation agent, and a clear printing is made.

[0013]

[Means for Solving the Problem] this invention receives the thermoplastic-polyester system resin (A) 100 weight section. the weight average molecular weight which is made to carry out the polymerization of the annular olefin shown by the following formula (I) or (II), and is obtained -- 800-7,000 -- and The resin film which makes a base material the resin constituent contained at a rate of the vinylene polymer (B) 5 of the annular olefin whose glass transition point is 120-270 degrees C, - 80 weight section The following formula which is temperature lower than the melting point of a component (A), and is extended and obtained at temperature lower than the glass transition point of the vinylene polymer of the

annular olefin of (B) component [0014]

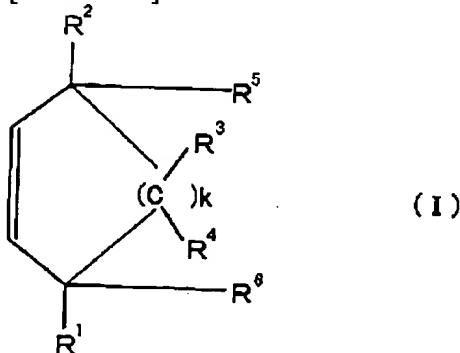
[Equation 2]

$$\text{空孔率 (\%)} = \frac{(延伸前のフィルムの密度 - 延伸後のフィルムの密度)}{\text{延伸前のフィルムの密度}} \times 100$$

[0015] It comes out and the porous film whose rate of a hole shown is 20 - 70% is offered.

[0016]

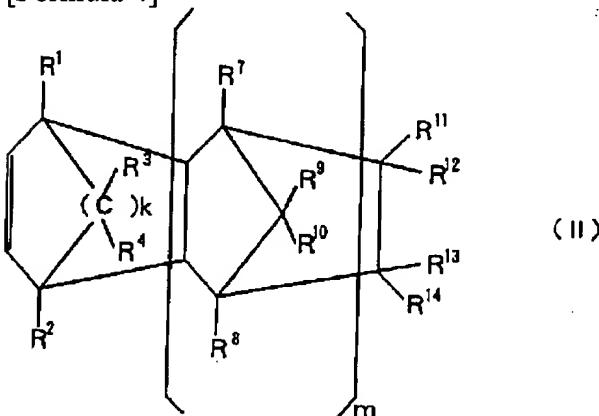
[Formula 3]



[0017] (R1-R4 show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) R5 and R6 are hydrogen atoms, and k is the integer of 0, or 1-4.

[0018]

[Formula 4]



[0019] (R1-R4, and R7-R14 show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) Either [R10 and] R11-R14 either [either / R9 and / R11-R14 and] may be connected mutually, and they may form the ring. k is the integer of 0, or 1-4. m is the integer of 0, or 1-8.

[0020]

[Embodiments of the Invention]

[1] 800 to less than 7,000 and a glass transition point make a detailed void form in the interior of a film by extending the film which makes a base material the resin constituent which contains other olefin system resins and a bisphenol type epoxy resin according to the vinylene polymer of the annular olefin which is 120 degrees C - 270 degrees C, and the need, and, as for the fine porosity polyester system resin film of a thermoplastic-polyester system resin constituent this invention, (A) thermoplastic-polyester system resin and (B) weight average molecular weight are obtained.

[0021] (A) The thermoplastic-polyester system resin used for a component:thermoplastic-polyester system resin this invention A kind or two sorts or more of a dicarboxylic acid or its low-grade alkyl

diester, For example, a terephthalic acid, an isophthalic acid, 2, 5, -, 2, 6- or 2, 7-naphthalene dicarboxylic acid, A succinic acid, a sebacic acid, an adipic acid, an azelaic acid, the biphenyl 4, a 4'-dicarboxylic acid, A hexahydro terephthalic acid, screw-p-carboxy phenoxy ethane, etc., Kind or glycols [two or more sorts of], for example, ethylene glycol, 1, 3-propanediol, neopentyl glycol, 1, and 4-cyclohexane dimethanol etc. can be manufactured according to condensation with a hydroxy acid as occasion demands. Moreover, the thermoplastic-polyester system resin used for this invention may be a block copolymer which consists of polyester which the polyester copolymer containing a mixed hydroxyl group and/or an ester plasticity acid radical is sufficient as, and is different. Desirable thermoplastic polyester resin is a polyethylene terephthalate, a polybutylene terephthalate, and polyethylenenaphthalate.

[0022] As a vinylene polymer of the annular olefin of the Component (B):polymer (B) component of an annular olefin The monocycle formula annular olefin shown by formulas (I), such as cyclobutenes, cyclopentenes, and cyclohexenes or the homopolymer of an annular olefin chosen out of the polycyclic formula annular olefin shown by formulas (II), such as norbornene and tricyclo-3-decene, -- or They are two or more sorts of mutual copolymers of this annular olefin. the weight average molecular weight (polypropylene conversion) 800 to less than 7,000 that 1,000-7,000, and whose glass transition temperature are 120 degrees C - 270 degrees C preferably -- desirable -- a 140-270-degree C thing -- a 170-270-degree C thing is mentioned especially preferably

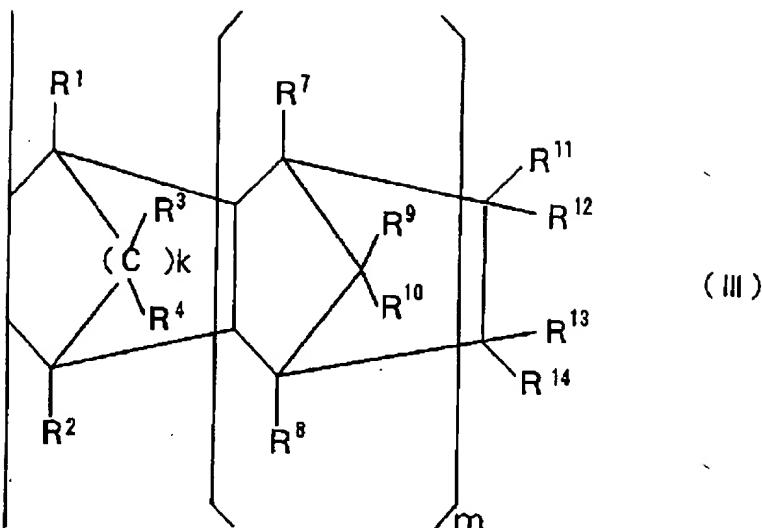
[0023] As an example of the above-mentioned annular olefin, a cyclobutene, a cyclopentene, Cyclopentenes, such as 4-methyl cyclopentene, a cyclohexene, The monocycle formula annular olefin; norbornene shown by front formulas (I), such as cyclohexenes, such as 3-methyl cyclohexene and 3-vinyl cyclohexene Norbornene, such as 1-methyl norbornene and 5-ethyl-2-norbornene Tricyclo-3-decene, such as tricyclo [4, 3, 0, 12.5]-3-decene and 2-methyl tricyclo [4, 3, 0, 12.5]-3-decene A dicyclopentadiene (tricyclo [4, 3, 0, 12.5]-3 and 7-deca diene or tricyclo [4, 3, 0, 12.5]-3, 8-deca diene), Dicyclopentadienes, such as 7-methyl dicyclopentadiene, tetracyclo [4, 4, 0, 12.5, 17.10]-3-dodecen, 8-methyl tetracyclo [4, 4, 0, 12.5, and 17.10]-3-dodecen, Tetracyclo-3-dodecen, such as 5 and 10-dimethyl tetracyclo [4, 4, 0, 12.5, and 17.10]-3-dodecen 6, 5, 1, 13.6, 02.7, ***** cyclo [09.13]-4-pentadecene, 6, 5, 1, 13.6, 02.7, 10-methyl ***** cyclo [09.13]-4-pentadecene, ***** cyclo pentadecene, such as 4, 7, 0, 12.5, 08.13, and ***** cyclo [19.12]-3-pentadecene ***** cyclo [6, 5, 1, 13.6, 02.7, 09.13]-4, 10-***** deca diene, Pentacyclo pentadecadiene, such as ***** cyclo [6, 5, 1, 13.6, 02.7, 09.13]-4 and 11-***** deca diene The polycyclic formula annular olefin shown by formulas (II), such as 6, 6, 1, 13.6, 110.13, 02.7, and hexa cyclo [09.14]-4-heptadecene, can be mentioned.

[0024] As a vinylene polymer of this annular olefin, that to which the polymerization gestalt carried out low-molecular quantification of the thing or these annular olefins polymer of a vinylene polymerization with the peroxide etc. is mentioned.

[0025] By using the organotransition metal compound of specialization [the vinylene polymer of the annular olefin by this vinylene polymerization gestalt], and an organic aluminum oxy-compound as a catalyst component, addition polymerization advances through the ethylene nature unsaturated bond of an annular olefin, a vinylene polymer is obtained, and the structure has the configuration unit shown in a following general formula (III) or a following formula (IV).

[0026]

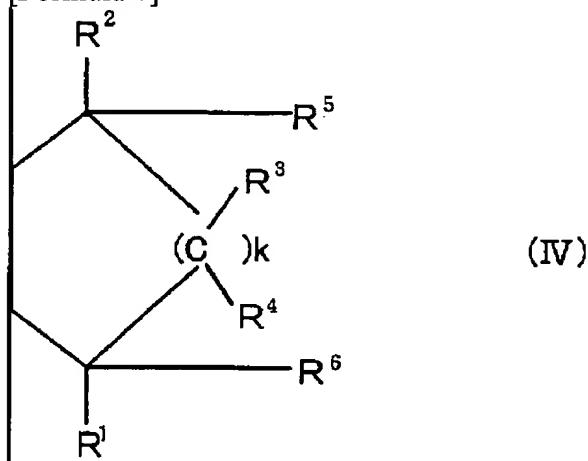
[Formula 5]



[0027] (R1-R4, and R7-R14 show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) Either [R10 and] R11-R14 either [either / R9 and / R11-R14 and] may be connected mutually, and they may form the ring. k is the integer of 0, or 1-4. m is the integer of 0, or 1-8. In addition, in a vinylene polymer, you may use the monomer from which R1-R14, and k and m are different by each monomer, respectively in the monomer unit expressed with this formula (III).

[0028]

[Formula 6]



[0029] (R1-R4 show independently the substituent containing the hydrocarbon group or halogen atom of a hydrogen atom and the carbon numbers 1-20 among a formula, respectively.) R5 and R6 are hydrogen atoms, and k is the integer of 0, or 1-4.

[0030] About the vinylene polymerization method of this annular olefin, although which technique, such as a slurry polymerization method, a vapor-phase-polymerization method, a bulk-polymerization method, a solution polymerization method, and a suspension-polymerization method, may be used for example, the slurry polymerization method, the solution polymerization method, and the bulk-polymerization method are suitable. Moreover, a batch type or continuous system is sufficient as a polymerization format.

[0031] After the bottom of presence of a monomer or un-existing may not be asked, but it may add in a polymerization system separately, respectively, and the organic transition compound and organic aluminum oxy-compound which are the constituent of the polymerization catalyst of this annular olefin may contact both within a polymerization system, may make a catalyst system form, they contact each

catalyst component beforehand before adding in a polymerization system, and they make a catalyst system form, you may introduce them in a polymerization system. There is especially no limit about the sequence in the case of contacting each catalyst component that a catalyst system should be made to form here, and it can be based on arbitrary sequence. Formation of a catalyst system can be performed by contacting each component under the inert gas ambient atmosphere for example, in an inert solvent. [0032] The following can be illustrated as a suitable example of the manufacture catalyst of the annular olefin polymer of this invention. That is, the catalyst system which comes to contain the catalyst component expressed with either of the following two general formulas and alumoxane is used suitably. [0033] (C₅R_n) X(C₅R_n) MeQ₂ or (C₅R_n) X_aY_bMeQ_{3-b} [0034] Me is four groups' transition metals, for example, Zr and Hf, among a formula, and ** (C₅R_n) is cyclopentadienyl or substitute cyclopentadienyl, and chooses R each from the group which differ and consists [an identity or] of hydrogen, the alkyl of carbon numbers 1-20, the alkenyl, an aryl, an alkyl aryl, or an arylated-alkyl machine. X is the alkylene or silicon of carbon numbers 1-4 which constructs across two rings (C₅R_n), or (C₅R_n) a ring and Y. a is the integer of 0, or 1-4, b is the integer of 0 or 1, and it is b=0 at the time of a=0. It differs, Q is [an identity or] the aryl of carbon numbers 1-20, an alkyl, the alkenyl, an alkyl aryl, an arylated-alkyl machine, an alkylidene machine, or a halogen each, and Y is oxygen, nitrogen, Lynn, or a sulfur atom. n shows the number of 0-4.

[0035] In addition, in case a polymerization is carried out using the above-mentioned catalyst, the vinylene polymer of the annular olefin of this invention can add a suitable quantity of hydrogen in order to obtain the polymer of desired molecular weight.

[0036] The domain of -78 degrees C - +150 degrees C of the temperature which carries out the polymerization of the annular olefin is usually -30 degrees C - +80 degrees C preferably. Moreover, the amount of the organotransition metal compound which is the constituent of a catalyst system, and the organic aluminum oxy-compound used is arbitrary within pertinent limits. for example, the case of a solution polymerization system -- the amount of the organotransition metal compound used -- 10⁻⁷, - 102 millimole / liter -- the domain of 10⁻⁴, - 10 millimole / liter is especially desirable The mole ratio of aluminum/transition metals usually has [the amount of the aluminum oxy-compound used] 10-100,000, and a desirable domain that is set especially to 100-10,000. The mole ratio of an annular olefin / above-mentioned transition-metals compound usually has [the amount of the annular olefin used] 1-1,000,000, and a desirable domain that is preferably set to 100-100,000. Moreover, as technique of adjusting the molecular weight of a polymer, selection of the modality of each catalyst component, the amount used, polymerization temperature, polymerization time, etc., the technique by the polymerization under hydrogen presence, etc. are mentioned further.

[0037] When using a polymerization solvent, petroleum fractions, such as aromatic hydrocarbons, such as alicycle group hydrocarbons, such as aliphatic hydrocarbon, such as halogenated hydrocarbons, such as polymerization solvent used from the former in this kind of polymerization method, for example, methylene chloride, 1, and 2-dichloroethane, a pentane, a hexane, a heptane, and an octane, a cyclopentane, and a cyclohexane, benzene, toluene, and a xylene, a gasoline, kerosene, and gas oil, or these mixed solvents can be used. Especially aromatic hydrocarbons are desirable also of these.

[0038] moreover, the weight average molecular weight (polypropylene conversion) which measured the molecular weight of the vinylene polymer of this annular olefin by the gel permeation chromatography (GPC) -- 800 to less than 7,000 -- desirable -- 1,000-7,000 -- it is the thing of the domain of 2,000-5,000 especially preferably The hole organization potency at the time of extension of a film becomes low less than by 800. If 7,000 is exceeded, an extension molding-temperature region will become narrow.

[0039] Moreover, the glass transition point (T_g) by measurement with the differential scanning type calorimeter of the vinylene polymer of this annular olefin is JIS. It is the midpoint glass transition temperature (T_{ms}) for which it is asked by the differential scanning type calorimetry according to 9-3 term of K 7121-1987, and 120 degrees C - 140-270-degree C 270 degrees C [170-270-degree C] are the thing of the domain of 200-270 degrees C especially preferably more preferably. Under in this domain, the hole formation at the time of film extension is not obtained, but if this domain is exceeded, the manufacture temperature of the resin constituent of a film base material will become high.

[0040] Of the vinylene polymer of these annular olefins, since the vinylene polymer of the polycyclic formula annular olefin which mainly used the annular olefin of a polycyclic formula demonstrates suitably broadening of the extension molding temperature of this invention, and the effect of occurrence of a hole, it is desirable.

[0041] As this polycyclic formula annular olefin polymer, the homopolymer of a polycyclic formula annular olefin, the mutual copolymer of a polycyclic formula annular olefin, or the mutual copolymer of a polycyclic formula annular olefin and a monocycle formula annular olefin is mentioned.

[0042] Moreover, of a polycyclic formula annular olefin, what used norbornene is easy for the molecular weight control at the time of a polymerization, and high polymerization activity is obtained and it is desirable. As this norbornene system polymer, the homopolymer of norbornene, the mutual copolymer of norbornene, or the mutual copolymer of norbornene and another annular olefin is mentioned.

[0043] Moreover, also of these norbornene system polymer, the homopolymer of norbornene and the mutual copolymer with norbornene and another annular olefin are desirable, and especially a norbornene homopolymer has highly desirable polymerization yield.

[0044] These annular olefin polymers can use the above-mentioned polymer as mixture which is independent or was mixed two or more sorts.

[0045] Moreover, in the vinylene polymer of this annular olefin, carrying out copolymerization to aromatic vinyl compounds, such as alpha1 olefins, such as ethylene and a propylene, styrene, and an alpha methyl styrene, etc. does not interfere in the domain which does not spoil the effect of this invention.

[0046] Since the denaturation olefin system resin (C) later mentioned to it since both compatibility other than the vinylene polymer (B) of a polyester system resin (A) annular olefin is raised in the film base material of this invention raises a film moldability and a low-molecular-weight-polyethylene resin (D) raises the moisture resistance of an extension resin film, it is desirable to blend a bisphenol A type epoxy resin (E).

[0047] Component (C): As an olefin system resin of an olefin system resin (C) component, weight average molecular weight can use the polyethylene of the shape of the letter of branching of 3, or a straight chain, poly (4-methyl pentene -1), a propylene independent copolymer, a propylene ethylene copolymer, a propylene ethylene butene-1 copolymer, ethylene and a vinyl acetate copolymer, and an ethylene-glycidyl-methacrylate copolymer 10,000-1,000,000, and the density of 0.86-0.97g/cm. having used these independently, or having used two or more sorts together, and having also denaturalized -- even when -- it is good Especially, the propylene system resin from the rigid field of a film is desirable.

[0048] In addition, as an olefin system resin which denaturalized, the graft copolymerization of the polar-group inclusion unsaturated compound is carried out to the above-mentioned olefin system resin. As a polar-group inclusion unsaturated compound for denaturalizing an olefin system resin, they are polar-group inclusion unsaturated compounds, such as a hydroxyl group, a carboxylic-acid machine, a carboxylic-acid anhydride machine, an epoxy group, and an amino group.

[0049] As an unsaturated compound containing a hydroxyl group, for example alpha, beta-unsaturation carboxylate, Namely, 2-hydroxyethyl (meta) acrylate, 2-hydroxy propyl (meta) acrylate, 2, 3-dihydroxy propyl (meta) acrylate, 2-hydroxymethyl-3-hydroxy propyl (meta) acrylate, 2 and 2-screw hydroxymethyl-3-hydroxy propyl (meta) acrylate, {, however (meta) acrylate the acrylic ester (meta) of the oligomer of the ethylene glycol of butanediol monochrome (meta) acrylate and the carbon numbers 4-40 etc. To} and the pan meaning acrylate and methacrylate, N-methylol acrylamide, To N-methylol methacrylamide and a pan, screw (2-hydroxyethyl) malate, Screw (2-hydroxy propyl) malate, screw (2, 3-dihydroxy propyl) malate, Screw (2-hydroxymethyl-2-hydroxy propyl) malate, Screw (2 and 2-screw hydroxymethyl-3-hydroxy propyl) malate etc., And the maleic acid or fumaric-acid ester of oligomer of the fumarate and the ethylene glycol of carbon numbers 4-40 which are these isomers, or a propylene glycol As mentioned above, when both carboxylic acids are not ester but one side of a hydroxyalkyl machine, it can illustrate as same compound. Furthermore, allyl alcohol, clo chill alcohol, 4-(2-hydroxyethyl) styrene, 3-(2-hydroxyethyl) styrene, 4-(hydroxymethyl) styrene, 3-(hydroxymethyl) styrene, 4-hydroxy styrene, 3-hydroxy styrene, etc. are mentioned. the above hydroxyl-group inclusion

unsaturated compound is independent -- or two or more sorts can be used together and it can use Of these, 2-hydroxyethyl (meta) acrylate and 2-hydroxy propyl (meta) acrylate are desirable.

[0050] As an unsaturated compound containing a carboxyl group, alpha, beta-unsaturated carboxylic acid, i.e., an acrylic acid, a methacrylic acid, a maleic acid, an itaconic acid, a citraconic acid, a butene dicarboxylic acid, a fumaric acid, a crotonic acid, an isocrotonic acid, etc. are mentioned, for example. Of these, they are an acrylic acid, a methacrylic acid, and a maleic acid preferably.

[0051] As an unsaturated compound containing a carboxylic-acid anhydride machine, an alpha, beta-unsaturation carvone acid-anhydride, maleic-anhydride, itaconic-acid-anhydride, anhydrous citraconic-acid, and anhydrous methyl (high *****) acid, an anhydrous acrylic acid, an anhydrous methacrylic acid, etc. are mentioned, for example. Of these, a maleic anhydride and itaconic acid anhydride are desirable.

[0052] As an example of the unsaturated compound containing an epoxy group A glycidyl methacrylate, metaglycidyl acrylate, N-{4-(2, 3-epoxy propoxy)-3, 5-dimethyl phenyl acrylamide, N-{4-(2, 3-epoxy propoxy)-3, 5-dimethyl phenyl methacrylamide, Allyl glycidyl ether, maleic-acid diglycidyl, maleic-acid methyl glycidyl, Maleic-acid ethyl glycidyl, maleic-acid isopropyl glycidyl, Maleic-acid t-butyl glycidyl, fumaric-acid diglycidyl, fumaric-acid methyl glycidyl, Fumaric-acid ethyl glycidyl, fumaric-acid isopropyl glycidyl, fumaric-acid t-butyl glycidyl, Itaconic-acid diglycidyl, itaconic-acid methyl glycidyl, itaconic-acid ethyl glycidyl, alpha, such as itaconic-acid isopropyl glycidyl, the epoxy-group inclusion derivative of beta-unsaturated carboxylic acid, 2-methylene glutaric-acid diglycidyl, 2-methylene glutaric-acid methyl glycidyl, 2-methylene glutaric-acid ethyl glycidyl, p-glycidyl styrene, etc. are mentioned. Of these, it is glycidyl-methacrylate, metaglycidyl acrylate, N-{4-(2, 3-epoxy propoxy)-3, and 5-dimethyl phenyl acrylamide preferably.

[0053] As an unsaturated compound containing the amino group, alpha and the amine inclusion alkyl ester of beta-unsaturated carboxylic acid, i.e., dimethyl aminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, a vinylpyridine, etc. are mentioned, for example.

[0054] 2-hydroxyethyl (meta) acrylate, 2-hydroxy propyl (meta) acrylate, a maleic anhydride, an acrylic acid, a methacrylic acid, a maleic acid, and the most desirable thing are 2-hydroxyethyl (meta) acrylate more preferably from the viewpoint of acquiring the fabricating-operation fitness of higher level in these polar-group inclusion unsaturated compounds.

[0055] The amount of grafts of this polar-group inclusion unsaturated compound is 0.5 - 3 % of the weight more preferably 0.2 to 5% of the weight 0.05 to 10% of the weight. At less than 0.05 % of the weight, if the compatible effect to a polyester system resin is small and exceeds 10 % of the weight, it will be easy to produce un-arranging -- the fluid failure at the time of the fabricating operation by a fall or gelation of the mechanical physical properties resulting from too much molecule disconnection of a polyester system resin becomes remarkable.

[0056] the amount of the polar-group inclusion unsaturated compound used used for a graft process -- an olefin system resin -- receiving -- 0.05 - 50 weight section -- it is 1 - 20 weight section preferably In under 0.05 weight section, since the required amount of grafts is not obtained, if the compatible effect of a polyester system resin is low and exceeds 50 weight section, it carries out [too much molecule disconnection or bridge formation of a polyester system resin is promoted, and / a difficulty may arise to fabricating-operation nature, or] the mechanical physical-properties fall of the mold goods and is not desirable.

[0057] As technique of denaturalizing an olefin system resin by the above-mentioned polar-group inclusion unsaturated compound, there is the technique of making it react under presence of radical occurrence agents, such as organic peroxide, or un-existing, technique of irradiating ultraviolet rays and a radial slit, or a method of making oxygen and ozone contact.

[0058] The above-mentioned denaturation olefin system resin is JIS when the denaturalizing olefin is polypropylene resin. MFR (230 degrees C, 2.16kg load) measured based on K-7201 has desirable 0.01-200g / 10 minutes, and is the thing of the domain for 0.1-100g / 10 minutes more preferably.

[0059] (D) The molecular weight of component:low-molecular-weight-polyethylene resin low molecular weight polyethylene is the thing of 1,000-8,000 preferably less than 10,000, and, specifically, a

polyethylene wax, paraffin, cull *****, etc. are mentioned.

[0060] (E) A component:bisphenol type epoxy resin bisphenol type epoxy resin has the desirable glycidyl ether type epoxy resin which is the reactant of bisphenol A, bisphenol F, bisphenol S, and epichlorohydrin. The weight per epoxy equivalent is [a weight per epoxy equivalent] bisphenol A type glycidyl ether of 500g [120-]/eq preferably below 2,000g / eq.

[0061] The film base material of an additional component this invention may contain the bulking agent, the pigment, the stabilizer, and ultraviolet ray absorbent other than above-mentioned (A) - (E) component. As an inorganic bulking agent, the calcium carbonate whose particle size is 0.05-5 micrometers, a silica, talc, a mica, a barium sulfate, a potassium silicate, a potassium titanate, etc. are mentioned. These are blended at a rate below 300 weight section to the sum sum 100 weight section of a resin.

[0062] the quantitative ratio of combination of each above-mentioned component which constitutes the resin constituent used for a composition ratio this invention -- the thermoplastic-polyester system resin 100 weight section of (A) component -- receiving -- the vinylene polymer of the annular olefin of (B) component -- 5 - 80 weight section -- 10 - 60 weight section comes out comparatively preferably, and it is blended

[0063] (A) The porous film with which the loadings of (B) component have the opacity which the void of sufficient amount for the interior of a film is not generated by extension, and is satisfied under in 5 weight section is not obtained to the component 100 weight section. Moreover, since a film moldability will fall and it will be easy to cause fracture at the time of extension of a film if it adds more mostly than 80 weight section, it is not desirable. Moreover, the oriented film which has sufficient thermal resistance is not obtained.

[0064] The extension resin film which makes a base material the following constituent other than the extension resin film which makes a base material the above-mentioned (A) component and (B) component can also be used. It is the fine porosity polyester system resin film which extends the vinylene polymer (B) 5 of an annular olefin - 80 weight section, and the resin film that makes a base material preferably 10 - 60 weight section, the olefine resin (C) 3 - 100 weight section, and the polyester system resin constituent that blended 5 - 40 weight section preferably, and is obtained to the thermoplastic-polyester system resin (A) 100 weight section.

[0065] As opposed to the thermoplastic-polyester system resin (A) 100 weight section The polymer (B) 5 of an annular olefin, - 80 weight section, Preferably 10 - 60 weight section, the olefin system resin (C) 3 - 100 weight section, Preferably 5 - 50 weight section and a low-molecular-weight-polyethylene resin (D) 1 - 10 weight section, It is the fine porosity polyester system resin film which extends the resin film which makes a base material preferably 2 - 7 weight section, the bisphenol type epoxy resin (E) 1 - 10 weight section, and the polyester system resin constituent that blended 2 - 7 weight section preferably, and is obtained.

[0066] (A) Under 3 weight section of the enhancement effect in opacity is [the loadings of (C) component to the component 100 weight section] inadequate, and the enhancement effect of a moldability is the parvus at the time of film molding. Moreover, if it adds more mostly than 100 weight section, a resin inversion of the matrix phase of (A) component in a constituent and (C) component will arise, an olefin system resin (C) serves as a matrix, and the fine porosity film which has sufficient thermal resistance is not obtained.

[0067] (A) The loadings of (D) component to the polyester system resin 100 weight section of a component occur a heat-resistant fall of the film obtained if enhancement of a moldability is not seen and 10 weight section is exceeded under in 1 weight section.

[0068] (A) The melting viscosity-down prevention effect by the moisture in the atmospheric air from which the loadings of (E) component to the polyester system resin 100 weight section of a component adsorbed into the constituent under in 1 weight section is the parvus. Moreover, when 10 weight section was exceeded and film molding is carried out, an interlaminar peeling (delamination) arises.

[0069] The extension resin film of the manufacture this invention of an oriented film (A) A thermoplastic-polyester system resin, the vinylene polymer of (B) annular olefin, The temperature which

exceeds the melting point of polyester resin for the resin constituent which contains (C) olefin system resin, (D) low-molecular-weight-polyethylene resin, and (E) bisphenol type epoxy resin as occasion demands using an extruder. By kneading at 260-300 degrees C, in a thermoplastic-polyester system matrix, for example, the polymer of an annular olefin, An olefin system resin and/or a denaturation olefin system resin, low molecular weight polyethylene, and a bisphenol type epoxy resin are distributed. Subsequently, this is extruded in the shape of a film, while thermoplastic polyester resin had existed by amorphous state from the die. Furthermore, this film is cooled to below the recrystallization temperature (for example, 60-120 degrees C) of a thermoplastic-polyester system resin. On the other hand, at least this preferably two to 10 times to ** at a direction of extrusion (MD) Two to 5 times, It extends two to 5 times crosswise (TD), and continuously, more than the recrystallization temperature (130-170 degrees C in for example, the case of a polyethylene terephthalate) of a polyester system resin, a heat set is performed at the temperature of under the melting point, and it is obtained by carrying out the recrystallization of the polyester resin.

[0070] In case the fine porosity polyester system resin film of this invention manufactures this, you may carry out the laminating of it to other resin layers. As other resin layers, polyamide resin, such as thermoplastic-polyester system resins, such as olefin system resins, such as an ethylene system resin and a propylene system resin, a polyethylene terephthalate, and a polybutylene terephthalate, nylon 6, and nylon 6 and 6, a polyvinyl chloride, polystyrene, etc. can be mentioned. Such other resin layers may contain bulking agents, such as a calcium carbonate, a titanium dioxide, clay, and a barium sulfate, in the resin constituent, and may contain UV agent and the antioxidation inhibitor 2 or less % of the weight in the resin constituent eight to 50% of the weight preferably zero to 50% of the weight. By a micro void occurring inside a film by extension, while an extension resin film is lightweighted, there is no translucence, an opacification is carried out, and the front face of an extension resin film is split-faced (matte). The grade of the split face is a domain for 400 - 4,500 seconds preferably about 100 to 6,000 seconds as a ***** exponent (JIS P-8119).

[0071] When the fine porosity polyester system resin film of this invention is a monolayer, the domain of 20-300 micrometers of the thickness of an extension resin film is 40-150 micrometers preferably. When using as a laminated film of the laminating more than a bilayer, it is 3-120 micrometers preferably, and other thickness is assigned as another layer and 1-150 micrometers is made to turn into 30-300 micrometers in the total thickness of a laminated film.

[0072] (3) The fine porosity polyester system resin film of an intended-use this invention is useful in itself as a poster form, drawing paper, a label paper, and a base material for carrying out a laminating to this extension resin film independence or pulp paper-milling paper, a polyethylene-terephthalate biaxial oriented film, etc., preparing a gelatin layer, a thermal recording coating layer, and a picture image acceptance record layer in this film front face, and using as printing paper, a thermographic recording paper, and hot-printing picture image acceptance paper.

[0073]

[Function] It has specific molecular weight, and since the annular olefin polymer (B) of specific structure carries out the detailed variance of what the melt viscosity at the time of extrusion carried out melting kneading of the mixture of near and both, and was used as the film into a thermoplastic-polyester system resin (A) matrix, while the vinylene polymer (B) and thermoplastic-polyester system resin (A) of an annular olefin of specific structure can make an extension temperature region large, a detailed void is generated by extending this. Moreover, the fine porosity polyester system resin film which has moderate opacity with an addition fewer than the addition of the conventional void formation agent (cavernous occurrence agent) is obtained.

[0074]

[Example] The example shown below explains this invention still concretely. In addition, the evaluation technique shown below estimated the evaluation in an example and the example of a comparison.

[0075] It is based on [I] evaluation technique opacity:JIS-P8138.

Pencil Note Nature: Apply a 200g load to the pencil of degree-of-hardness H set so that it might become perpendicular to the obtained extension resin film using Pencil hardness meter (scratch circuit tester) by

the Oriental energy machine Company, and draw a segment at 200 seconds/m of speeds. Visual observation of this segment is carried out, and it is judged as follows.

O : it can read clearly.

**: Although the note of is done, it is thin and is hard to read.

x: -- it is hardly written down

Curl Height: The extension resin film was cut out to 200mm long and 200mm wide, and it considered as the test piece. The test print of the test piece was carried out with the LASER beam printer (canon A404GII), and face-up **** (a printing side is facing up) was performed.

Since it became timeout time, translation result display processing is stopped.